

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 114 735 A2**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
11.07.2001 Bulletin 2001/28

(51) Int Cl.7: **B41M 5/00**

(21) Application number: **01400032.7**

(22) Date of filing: **08.01.2001**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(72) Inventor: **Monie, Sanjay A.**
Silver Spring, MD 20910 (IN)

(74) Representative: **Portal, Gérard et al**
Cabinet Beau de Loménie
158, rue de l'Université
75340 Paris Cédex 07 (FR)

(30) Priority: **06.01.2000 US 478520**

(71) Applicant: **WESTVACO CORPORATION**
New York New York 10171 (US)

(54) **Glossy inkjet coated paper and process of making it**

(57) The inkjet recording sheet of the present invention comprises a cellulosic support, e.g., paper, having applied to at least one surface thereof one or more base coats, to provide a high absorption capacity for the ap-

plied inks, and an ink receptive top coat applied over the base coat(s) that is capable of being finished to a high gloss, comparable to a cast coated sheet, without sealing the surface.

EP 1 114 735 A2

BEST AVAILABLE COPY

DescriptionBackground of Invention

- 5 [0001] The present invention relates generally to an inkjet recording sheet, and more particularly to an inkjet recording sheet having an ink receptive coating that is subject to being finished to a high gloss comparable to a cast coated sheet.
- [0002] Paper for inkjet recording sheets used in inkjet printing must rapidly absorb the ink vehicle (e.g., water or solvent), to reduce drying time. Further, diffusion of ink laterally on the surface of the recording sheet must be prevented in order to achieve high resolution without bleeding or feathering. Moreover, a coated paper for inkjet printing should
- 10 be able to achieve these results without any substantial dimensional changes. For this purpose, the base paper for inkjet sheets is generally made from bleached chemical pulp to which fillers, dyes, and if required, sizing agents and strength enhancers are added. An example of a typical base paper for use in the manufacture of an inkjet recording sheet is disclosed in U.S. Patent No. 5,985,424 assigned to the present assignee herein.
- [0003] It is also known that paper substrates for inkjet recording can be improved by applying a base coating to the paper surface before applying the ink receptive coating. Such base coats generally comprise a pigment and binder to
- 15 produce a coated surface that has a porous structure with a large number of pores or voids. An example of a base coat for an inkjet recording sheet is also disclosed in U.S. Patent No. 5,985,424.
- [0004] Meanwhile, the ink receptive coatings for inkjet paper must provide a surface that is receptive to the inks used for printing. In the past, this result has been achieved through the use of high pigment-to-binder ratios, usually in combination with conventional pigments and other coating materials to provide a porous and permeable coating layer. However, because of the highly specific requirements for inkjet printing, conventional coating materials used in other printing processes generally are unsatisfactory for inkjet printing. This is especially true in the case of the development of inkjet recording paper for high quality printing, e.g., glossy inkjet paper that looks and feels like a photograph for producing near photographic images using OEM (Original Equipment Manufacturers) inkjet printers. In this regard,
- 20 image quality is determined by the roundness, color uniformity and sharpness of the boundaries of the ink dots applied to the substrate substantially as disclosed in U.S. Patent No. 4,877,686. In order to meet these requirements, new pigments and binders have been developed specifically for use in ink receptive coatings.

Summary of Invention

- 30 [0005] It is a general object of the present invention to provide a high gloss inkjet recording sheet that has superior performance during inkjet printing.
- [0006] More particularly, it is an object of the present invention to provide a high gloss inkjet recording sheet capable of use in OEM printers to make high quality prints with near photographic image quality.
- 35 [0007] In the past, cast coating has been utilized to make inkjet recording paper with a high gloss. This method has been practiced either using a pigmented coating as shown for example in U.S. Patents Nos. 5,281,467; 5,397,619; 5,567,513; and 5,863,648, or with a polymeric coating as shown for example in U.S. Patents Nos. 5,670,242 and 5,741,584 often with a base coat to provide drainage and curl control. The methods utilizing pigmented coatings employ for the most part silica pigments, and while such coatings yield a high gloss and a photographic feel upon cast coating,
- 40 the ink dots applied to such sheets tend to be illdefined and nonuniform in color and roundness. Meanwhile, the polymer based coatings used in cast coating typically produce good ink dot characteristics, but they are slow to dry yielding prints that are tacky to the touch and produce undue coalescence. However, because cast coating is a slow process which requires large capital and operating costs, there remains a need in the art to provide a high gloss inkjet recording sheet that can be manufactured by more conventional methods with the capability of producing photographic-like images for high quality printing. To satisfy this need, the inkjet recording sheet of the present invention was developed.
- 45 [0008] Accordingly, the first object of the present invention is a process for producing a glossy inkjet recording sheet which comprises:
- a) applying onto at least one surface of a paper substrate a first base coating consisting essentially of pigment and binder;
 - 50 b) applying over said first base coating an ink receptive top coating consisting essentially of pigment and binder; and,
 - c) finishing the coated surface to achieve a 60 degree gloss of at least about 60 as measured by the ASTM Method D523 and a Distinctness of Image (DOI) of at least about 30.

- 55 [0009] According to a first feature of the process of the invention, a second base coating is applied over the first base coating before the application of the ink receptive top coating.
- [0010] In a preferred embodiment, in the process of the invention, the paper substrate is an alkaline paper having a

basis weight in the range of 100-150g/m² and an caliper of at least about 5.0 mil; the first base coating comprises essentially precipitated calcium carbonate and calcined clay, as pigments, dispersed in a binder which at a concentration of about 10-15% by weight of the total weight of the first base coating; the ink receptive top coating comprises essentially fumed alumina having a primary particle size on the order of about 13 nanometers and a specific surface area less than about 75m²/g dispersed in a binder which is at a concentration of about 5-10 weight % of the total weight of the ink receptive top coating; and the coated surface of step (c) is finished in a calendar device at a moisture content of from about 6-8%, a nip load of from about 600-800 pli, with a hot roll temperature of from about 100-200 degrees F.; one-to-six nips.

[0011] According to another feature of the process of the invention, said pigments of said first base coating comprise up to about 25 parts by weight of precipitated silica for improved absorptivity of the applied inks.

[0012] In this latter case, preferably said precipitated silica replaces the corresponding weight parts of calcium carbonate pigment.

[0013] Alternatively, in the process of the invention, said pigments of said first base coating comprise up to about 25 parts by weight of silica gel for improved absorptivity of the applied inks.

[0014] In this latter case, preferably said silica gel replaces the corresponding weight parts of calcium carbonate pigment.

[0015] Another object of the invention is a glossy inkjet recording sheet comprising as the substrate, paper, having applied to at least one surface thereof a first base coating comprising essentially precipitated calcium carbonate and calcined clay pigments dispersed in a binder at a concentration of about 10-15 weight % of binder, and an ink receptive top coating applied over said base coating comprising essentially fumed alumina having a primary particle size on the order of about 13 nanometers and a specific surface area less than about 75 m²/g dispersed in a binder which is at a concentration of about 5-10% binder, wherein the finished coated surface of said recording sheet has a 60° gloss of at least about 60 according to ASTM Method D523 and a Distinctness of Image (DOI) measurement of at least about 30.

[0016] According to a first characteristic of the inkjet recording sheet of the invention, up to 25 parts by weight of the calcium carbonate pigment in the first base coating is replaced with silica.

[0017] According to a second characteristic of the inkjet recording sheet of the invention, a second base coating is applied over said first base coating and up to 25 parts by weight of the calcium carbonate pigment in the first base coating is replaced with silica.

[0018] Preferably the an inkjet recording sheet of the invention is prepared using an alkaline base paper that is size pressed to achieve suitable water resistance. In a preferred embodiment of the present invention, one or more base coatings and an ink receptive top coating are applied to one or both sides of the base paper. The top coating preferably includes a fumed (pyrogenic) alumina with polyvinyl pyrrolidone as the binder. The base coatings preferably comprise precipitated calcium carbonate and calcined clay pigments with polyvinyl acetate binder. Where a single base coating is employed, or in the case of double base coatings, the first applied, or lower base coat, may also contain silica to increase ink vehicle absorbency. Calendering such a product at high moisture yields a 60° sheet gloss of at least 60 as determined by ASTM Method D523 "Measurement of Specular Gloss", which is comparable to a cast coated sheet. The finished sheets prepared in this manner have a DOI (Distinctness of Image) rating of at least 30, which is comparable to silver-halide glossy photographic paper. DOI is a measure of the reflective resolving power of a surface, and correlates closely with a photographic surface finish. The instrument used to measure this parameter (I²R Gloss Box "Distinctness of Image" Meter), consists of a light box with a test pattern of open circles of different sizes, ranked 10 for the largest and 100 for the smallest. The light box is mounted on a stand face-down, and the sheet to be tested is placed coated side up underneath the stand. The reflection of the incomplete circles on the sheet is viewed, and the value is reported as the smallest circle where it is still apparent that the circles are not closed. The smaller the circle (i.e., higher the value), the greater the reflective value of the coated surface. DOI correlates better with the subjective perception of gloss than the measurement of specular gloss. Such products have been found to be printable in all existing OEM desktop printers to yield high quality, photographic-like prints. The printed sheets are not tacky or rough to the touch, they are quick drying (less than 60 seconds), and the ink dots are round, with sharp boundaries and uniform color density.

[0019] As used in the present invention, fumed alumina is alumina that has been formed by the high temperature hydrolysis of gaseous aluminum trichloride so that it forms highly pure alumina particles. These particles have a nanometer scale primary particle size (average about 13 nm), with a very narrow particle size distribution. While these particles have no internal surface, they have a very high surface area-to-volume ratio and tend to have a specific surface area of about 75 m²/g. Unlike fumed silica, which has an anionic surface charge and which tends to be amorphous, fumed alumina has a cationic surface charge and is crystalline in form. The high specific surface area with a lot of accessible cationic sites helps to fix the anionic inkjet dyes and the crystalline nature of the particles contributes to the glossing potential of the coated surface.

[0020] The use of fumed alumina in inkjet coatings is known as shown, for example, in U.S. Patent No. 5,171,626, and is to be contrasted with the hydrated aluminas disclosed for use in inkjet coatings by the prior art for example in

U.S. Patents Nos. 5,635,291; 5,846,647; and 5,869,177.

Detailed Description

- 5 **[0021]** The base paper for the inkjet recording sheet of the present invention is preferably an alkaline paper having a basis weight in the range of 100-150 g/m² with a caliper of at least about 5.0 mil. It is prepared from a bleached wood pulp furnish to which is added a sizing agent such as alkylketene dimer, and fillers such as precipitated calcium carbonate and calcined clay. An example of a suitable precipitated calcium carbonate is ALBAGLOS supplied by Specialty Minerals. An example of a suitable calcined clay is ANSILEX supplied by Englehard Chemical Company. The base
10 paper thus formed is preferably size pressed with a mixture of starch and styrene maleic anhydride in a conventional manner. Finished base paper properties (typical values) are, caliper greater than 5.0 mils, and preferably about 5-8 mils; TAPPI opacity of about 85-95%; TAPPI brightness of about 80-95%; Sheffield smoothness of about 150-300 seconds (units are approximately equivalent to cubic centimeters of air per minute times 10); and a Hercules size of about 300-900 seconds. This base paper is particularly advantageous for the novel inkjet sheet of the present invention because it provides exceptional dimensional stability during use.
- 15 **[0022]** The preferred base coatings for the inkjet recording sheet of the present invention are prepared from a formulation comprising a mixture of precipitated calcium carbonate (PCC) and calcined clay dispersed in a binder preferably comprising polyvinyl acetate. The PCC pigment is incorporated into the coating formulation at a dry weight of from 40-60%. Calcined clay is incorporated into the coating formulation at a dry weight of from about 20-30%. Up to about
20 25 parts by weight of the calcium carbonate may be replaced with silica gel W-300 (supplied by Grace Company), or precipitated silica FK-310 (supplied by Degussa). When more than one base coating is used, only the first applied or lower based coat preferably includes silica. The addition of silica improves the drying time of the ink and provides increased ink density. Typical binders for the base coating include polyvinyl acetate (about 10-15%), an example of which is Vinac 848 supplied by Air Products or other suitable binders such as polyvinyl alcohol. In addition to these basic ingredients, there may be added sufficient ammonium hydroxide to dissolve the protein and a thickener such as AL-
25 COGUM L28 (supplied by Alco Chemical Company) to reach the target viscosity. A viscosity in the range of from about 3000-4000 centipoise Brookfield (20 rpm, No. 4 spindle) is preferred at a solids content of about 50-60%. The base coating or coatings are applied to the paper to achieve a total coat weight within the range of about 7-20 lbs/ream (ream size 3300 ft²), each side using any conventional coating device known to those skilled in the art (blade coater preferred).
- 30 **[0023]** The ink receptive coating for the inkjet recording paper of the present invention is applied directly over the base coat or coatings. It is designed to provide a high glossing surface yielding superior printed images. The ink receptive coating is prepared from a formulation comprising fumed (pyrogenic) alumina with a nanometer scale particle size of 50-100 nm and a very narrow particle size distribution. Up to 40% of the fumed alumina may be replaced with
35 cationic colloidal silica (e.g., Eka Bindzil-Cat 80); alumina hydrate (e.g., Alcoa Hydral Coat); or, boehmite alumina (e.g., Alcoa HiQ-40). These pigment components are dispersed in a binder consisting essentially of polyvinyl pyrrolidone (e.g., ISP PVP K-60). Other suitable ink receptive coating binders comprise partially or fully hydrolyzed, low-to-medium molecular weight polyvinyl alcohols (e.g., Air Products 107, 203, 205 or 310). The binder is added at a level of between about 5-10 parts on 100 parts pigment.
- 40 **[0024]** The water fastness and image color accuracy of the ink receptive coating can be enhanced by the addition of up to 5 parts (based on 100 parts pigment) of a polycationic material such as poly-DADMAC (e.g., Nalco 7544). If necessary, the coating can be thickened with suitable thickeners such as CMC or hydroethyl-cellulose (e.g., National 250 MR) to achieve a viscosity appropriate for the coating method employed.
- 45 **[0025]** The ink receptive top coating can be applied using air-knife, flexography, or rod/blade metering at a coat weight of between about 2-6 lbs/ream (ream size 3300 ft²). The targeted sheet moisture after coating is between about 4-8%. The final sheet is glossed by finishing in a super calender device at high moisture (6-8%), at a load of about 600-800 pli, 110-300°F hot roll temperature, one-to-six nips, at a speed of from 100-450 fpm.
- 50 **[0026]** Inkjet recording sheets prepared in accordance with the foregoing description have been found to provide superior performance with a variety of inkjet inks and inkjet printers. In addition, as demonstrated by the results shown in the following table, the DOI of the inkjet recording sheet of the present invention identified as "Prototype" is equivalent to typical glossy photographic papers presently on the market and to the best cast coated inkjet products current available.

Table

Sample	60% Gloss	DOI
PROTOTYPE	61	30

Table (continued)

Sample	60% Gloss	DOI
Inkjet Paper		
HP Premium Photo	91	20
Konica Photo Glossy (cast coated)	90	30
Kodak Inkjet Photo	80	10
Great White Glossy Photo	80	0
Hammermill Jet Print Ultragloss	68	0
Hammermill Jet Print Photo	84	20
Canon Glossy Photo	24	0
Epson Photo Quality Glossy	41	0
Avery Glossy Photo Quality	44	0
Computjet Photo Glossy	54	0
IBM Gloss Coated	66	10
IBM Digital Photo	64	10
Xerox Photo Gloss	89	20
Champion Inkjet High Gloss	88	10
Lexmark Inkjet Photo (cast coated)	30	30
Comp USA Inkjet Photo	66	20
Photographic Papers		
Kodak Porta Glossy	80-93	30
Kodak Supra Glossy	86-91	30
Kodak Ultra Glossy	90	30

[0027] Although only a preferred embodiment of the present invention has been fully disclosed herein, those skilled in the art will understand that various changes and modifications may be made in the invention as disclosed without departing from the spirit of the invention as defined in the appended claims.

Claims

1. A process for producing a glossy inkjet recording sheet which comprises:

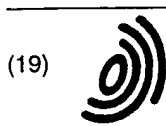
- applying onto at least one surface of a paper substrate a first base coating consisting essentially of pigment and binder;
- applying over said first base coating an ink receptive top coating consisting essentially of pigment and binder; and,
- finishing the coated surface to achieve a 60 degree gloss of at least about 60 as measured by the ASTM Method D523 and a Distinctness of Image (DOI) of at least about 30.

2. The process of claim 1 wherein a second base coating is applied over the first base coating before the application of the ink receptive top coating.

3. The process of claim 1 or 2 wherein:

- said paper substrate is an alkaline paper having a basis weight in the range of 100-150 g/m² and a caliper of at least about 5.0 mil;
- said first base coating of step (a) comprises essentially precipitated calcium carbonate and calcined clay, as pigments, in a binder, the binder representing about 10-15% of weight of the total weight of the first base coating;
- said ink receptive top coating of step (b) comprises essentially fumed alumina pigment having a primary particle size on the order of about 13 nanometers and a specific surface area less than about 75m²/g dispersed in a binder at a concentration of about 5-10% by weight of the total weight of the ink receptive top coating; and

- said coated surface of step (c) is finished in a calender device at a moisture content of from about 6-8%, a nip load of from about 600-800 pli, with a hot roll temperature of from about 100-200 degrees F., one-to-six nips.
4. The process of anyone of claims 1 to 3 wherein said pigments of said first base coating comprise 25 parts by weight of precipitated silica for improved absorptivity of the applied inks.
 5. The process of claim 4 wherein said precipitated silica replaces the corresponding parts by weight of a calcium carbonate pigment.
 6. The process of claims 1 to 3 wherein said pigments of said first base coating comprise up to about 25 parts by weight of silica gel for improved absorptivity of the applied inks.
 7. The process of claim 6 wherein said silica gel replaces the corresponding parts by weight of calcium carbonate pigment.
 8. A glossy inkjet recording sheet comprising as the substrate, paper, having applied to at least one surface thereof a first base coating comprising essentially precipitated calcium carbonate and calcined clay dispersed in binder at a concentration of about 10-15% binder, and an ink receptive top coating applied over said base coating comprising essentially fumed alumina having a primary particle size on the order of about 13 nanometers and a specific surface area less than about 75 m²/g dispersed in a binder at a concentration of about 5-10% binder, wherein the finished coated surface of said recording sheet has a 60° gloss of at least about 60 according to ASTM Method D523 and Distinctness of Image (DOI) measurement of at least about 30.
 9. The inkjet recording sheet of claim 6 wherein up to 25 parts by weight of the calcium carbonate pigment in the first base coating is replaced with silica.
 10. The inkjet recording sheet of claim 6 wherein a second base coating is applied over said first base coating and up to 25 parts by weight of the calcium carbonate pigment in the first base coating is replaced with silica.



(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 114 735 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
12.09.2001 Bulletin 2001/37

(51) Int Cl.7: **B41M 5/00**

(43) Date of publication A2:
11.07.2001 Bulletin 2001/28

(21) Application number: **01400032.7**

(22) Date of filing: **08.01.2001**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**
Designated Extension States:
AL LT LV MK RO SI

(72) Inventor: **Monie, Sanjay A.**
Silver Spring, MD 20910 (IN)

(74) Representative: **Portal, Gérard et al**
Cabinet Beau de Loménie
158, rue de l'Université
75340 Paris Cédex 07 (FR)

(30) Priority: **06.01.2000 US 478520**

(71) Applicant: **WESTVACO CORPORATION**
New York New York 10171 (US)

(54) **Glossy inkjet coated paper and process of making it**

(57) The inkjet recording sheet of the present invention comprises a paper support, having applied to at least one surface thereof a first coating comprising precipitated calcium carbonate and calcined clay dispersed in binder, an ink receptive coating comprising fumed alumina dispersed in binder. The ink receptive coating is

capable of being finished to a high gloss, comparable to a cast coated sheet, without sealing the surface.

Process of producing inkjet recording sheet comprising on paper substrate, on at least one surface: a) a first coating of pigment and binder, b) an ink receptive coating of pigment and binder, c) finishing to achieve high gloss.

EP 1 114 735 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 40 0032

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 949 120 A (REXAM INDUSTRIES) 13 October 1999 (1999-10-13)	1,2	B41M5/00
Y	* page 3, line 12 - line 22 * * page 3, line 49 - line 51 * * page 4, line 31 - line 58 * * page 5, line 23 - line 28 * * page 8, line 44 - line 47 * * page 9, line 20 - line 25; figure 1 *	3-10	
Y	WO 99 56965 A (ENGELHARD) 11 November 1999 (1999-11-11) * page 2, line 20 - line 24 * * page 7, line 25 - page 8, line 8 * * page 10, line 3 - line 5 * * page 10, line 30 - page 11, line 1 * * page 12, line 5 - line 10; claims 1,10,17 *	4-7,9,10	
D,Y	US 5 985 424 A (DEMATTE ET AL.) 16 November 1999 (1999-11-16) * column 2, line 27 - line 32 * * column 2, line 38 - line 65 * * column 3, line 58 - line 64 * * column 4; table I * * column 4, line 65 - line 67 *	3,8	
Y	EP 0 331 125 A (CANON) 6 September 1989 (1989-09-06) * page 3, line 43 - line 50 * * page 4, line 1 - line 2 * * page 6, line 7 - line 16 * * page 6, line 49 - line 50 * * page 10, line 23 - line 29 * * page 11, line 1 - line 13 * * page 13, line 28 - line 35 *	3,8	TECHNICAL FIELDS SEARCHED (Int.Cl.7) B41M
-/--			
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10 July 2001	Examiner Magrizos, S
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03.02 (P04C01)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 40 0032

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Y	DE 35 37 706 A (CANON) 24 April 1986 (1986-04-24) * page 7, line 1 - line 19 * * page 16, line 13 - page 18, line 6 * * page 22, line 1 - line 14 * * page 32, line 16 - line 19 * * page 33; table I * * page 35; table II *	3,8	
Y	US 4 102 845 A (SCHRÖDER ET AL.) 25 July 1978 (1978-07-25) * column 1, line 53 - column 2, line 17 * * column 3, line 40 - column 4, line 61 *	3	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
Place of search THE HAGUE		Date of completion of the search 10 July 2001	Examiner Magrizos, S
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/82 (P/M/C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 40 0032

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

10-07-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 949120 A	13-10-1999	BR 9901251 A	08-03-2000
		JP 11342567 A	14-12-1999
WO 9956965 A	11-11-1999	US 5997625 A	07-12-1999
		AU 3563599 A	23-11-1999
		BR 9910165 A	09-01-2001
		CN 1301218 T	27-06-2001
		EP 1079977 A	07-03-2001
US 5985424 A	16-11-1999	NONE	
EP 331125 A	06-09-1989	JP 2198889 A	07-08-1990
		AT 111818 T	15-10-1994
		AU 626290 B	30-07-1992
		AU 3098789 A	07-09-1989
		CA 1337388 A	24-10-1995
		CA 1337321 A	17-10-1995
		DE 68918307 D	27-10-1994
		DE 68918307 T	18-05-1995
		DK 103789 A	05-09-1989
		ES 2059591 T	16-11-1994
		FI 891040 A,B,	05-09-1989
		NO 301410 B	27-10-1997
		US 5266383 A	30-11-1993
		JP 2043083 A	13-02-1990
		JP 2694771 B	24-12-1997
DE 3537706 A	24-04-1986	JP 61100491 A	19-05-1986
		JP 2066072 C	24-06-1996
		JP 5036237 B	28-05-1993
		JP 61135783 A	23-06-1986
		JP 61143175 A	30-06-1986
		JP 61148090 A	05-07-1986
		GB 2167973 A,B	11-06-1986
		HK 32491 A	03-05-1991
US 4102845 A	25-07-1978	US 4664952 A	12-05-1987
		DE 2442704 A	25-03-1976
		CA 1043033 A	21-11-1978
		CH 596381 A	15-03-1978
		FI 752489 A	07-03-1976
		FR 2283990 A	02-04-1976
		NL 7510507 A	09-03-1976
		NO 752327 A	09-03-1976
		SE 7509900 A	08-03-1976

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☒ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☒ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.